METHOD FOR STORING HYDROGEN, HYDROGEN CLATHRATE COMPOUND AND PRODUCTION METHOD THEREOF

CROSS REFERENCE TO RELATED APPLICATION

[0001] This is a continuation application of PCT/JP03/07318 filed on June 10, 2003.

FIELD OF THE INVENTION

[0002] The present invention relates to a method for storing hydrogen capable of achieving the relatively light-weight and stable storage of hydrogen at or near the ordinary temperature and the ambient pressure and allowing easy takeoff of the stored hydrogen and also to a hydrogen clathrate which contains hydrogen and a production method thereof.

BACKGROUND OF THE INVENTION

[0003] Recently, new clean energy systems in which hydrogen is used as an energy medium have been proposed as a countermeasure against global environmental problems due to emission of CO_2. Among such energy systems, fuel cell is based on an energy conversion technology of taking electric energy out of hydrogen and oxygen by converting chemical energy, produced when hydrogen and oxygen react with each other to form water, into electric energy. This technology draws attention as the most important next-generation technology to be used as a power source alternative to gasoline engine for vehicles, an on-site electric generator for household use, and a DC power supply for IT (information technology) use.

[0004] However, the biggest problems of the hydrogen fuel are storage and transport thereof.

[0005] There are various methods have been proposed as method for storing hydrogen. As one of the methods, there is a method of storing hydrogen in gaseous phase into a high-pressure gas cylinder. This storage at high pressure is simple, but requires a container having thick wall. Accordingly, the container is so heavy that the efficiency of storage and transport is poor. Therefore, for example, the application to automobiles is difficult because weight saving counts in automobile manufacture. On the other hand, in case of storing hydrogen in liquid phase, the efficiency of storage and transport is improved as compared to the storage in gaseous phase. However, high-purity hydrogen is required to make the hydrogen in liquid phase and a special container capable of withstanding cryogenic temperature because the temperature of liquefaction process is an extremely low temperature of -252.6 °C. That is, there is economical problem. There is another proposal of using hydrogen storage alloy. However, there are problems that the alloy itself is heavy and that, in case of Mg based hydrogen storage alloy having lighter weight, the temperature for emitting stored hydrogen is high near 300 °C. There is further another proposal of using porous carbon material such as carbon nanotube. However, there are a lot of problems that the repeatability of hydrogen storage is low, that the storage under high pressure condition is required, that it is difficult to manufacture carbon nanotubes, and the like.

[0006] It is an object of the present invention to provide a method of storing hydrogen to be useful as a novel storage and transport method capable of solving the aforementioned problems of the prior art, and capable of achieving the relatively light-weight and stable storage of hydrogen at or

near the ordinary temperature and the ambient pressure and allowing easy takeoff of the stored hydrogen.

[0007] It is another object of the present invention to provide a hydrogen clathrate to be useful as a novel storage and transport method capable of solving the aforementioned problems of the prior art, and which is relatively light weight and can store hydrogen at or near the ordinary temperature and the ambient pressure and to provide a production method thereof.

SUMMARY OF THE INVENTION

[0008] The method for storing hydrogen of the present invention is characterized in that organic compound is brought into contact with hydrogen gas in a pressurized state.

[0009] Organic compounds which can be used in the present invention do not include organic compounds consisting of carbon atoms only such as graphite, carbon nanotube, and fullerene and include organic metallic compounds containing metallic component. The organic compound is basically solid, but may be liquid if it can enclose hydrogen in the pressurized state. In case of solid organic compound, it may be in crystalloid form or in amorphous form.

[0010] Through hard studies about method for storing hydrogen, the inventor of this invention found that easy storage of hydrogen can be achieved by bringing hydrogen gas into contact with the organic compound in a pressurized state to form a hydrogen molecular compound which is relatively light weight and can stably hold hydrogen at or near the ordinary temperature and the ambient pressure.

[0011] The molecular compound used in the present invention

means a compound composed of two or more kinds of compounds each of which can stably exist alone in which such compounds are combined by relatively weak interaction, other than covalent bond, as typified by hydrogen bond and van der Waals force. Examples of such compounds include hydrate, solvate, addition compound, and clathrate. The hydrogen molecular compound as mentioned above can be formed by bringing organic compound capable of forming a hydrogen molecular compound into contact with hydrogen under a pressurized condition so as to react. The hydrogen molecular compound is relatively light weight and can store hydrogen at or near the ordinary temperature and the ambient pressure and allows emission of hydrogen therefrom by a simple method such as heating.

[0012] The hydrogen molecular compound according to the present invention may be a hydrogen clathrate in which hydrogen molecules are enclosed by contact reaction between organic compound and hydrogen molecules.

[0013] The hydrogen clathrate of the present invention is characterized in that hydrogen is enclosed by contact reaction between host compound and hydrogen.

[0014] By the contact reaction between host compound and hydrogen, the hydrogen can be selectively and stably enclosed in the host compound so that the hydrogen can be stored at the ordinary temperature and the ambient pressure and the stored hydrogen can be emitted at a relatively low temperature.

[0015] In the present invention, the host compound is preferably a host compound of multimolecular type, especially a phenol type host compound or an imidazole type host compound.

[0016] A production method of a hydrogen clathrate of the present invention is characterized by dissolving a host

compound into a solvent, recrystallizing the host compound with injecting hydrogen into the solvent, and inserting hydrogen molecules into crystal lattice of the host compound. According to this method, the hydrogen clathrate in which hydrogen is enclosed into the host compound can be effectively produced at the ordinary temperature and the ambient pressure.

[0017] A production method of a hydrogen clathrate according to another embodiment of the present invention is characterized by bringing hydrogen gas into contact with a host compound in a pressurized state.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] FIG. 1 is a graph showing the evaluation result of hydrogen storage performance of BHC in Example 1;

FIG. 2 is a graph showing the evaluation result of hydrogen storage performance of BHC in Example 2;

FIG. 3 is a graph showing the evaluation result of hydrogen storage performance of BA in Example 3;

FIG. 4 is a graph showing the evaluation result of hydrogen storage performance of THPEY in Example 4;

FIG. 5 is a graph showing the evaluation result of hydrogen storage performance of TMPE in Example 5;

FIG. 6 is a graph showing the evaluation result of hydrogen storage performance of TPE in Example 6;

FIG. 7 is a graph showing the evaluation result of hydrogen storage performance of DBDCA in Example 7;

FIG. 8 is a graph showing the evaluation result of hydrogen storage performance of FBDCA in Example 8;

FIG. 9 is a graph showing the evaluation result of hydrogen storage performance of TPBDM in Example 9;

FIG. 10 is a graph showing the evaluation result of hydrogen storage performance of TPHDD in Example 10;

FIG. 11 is a graph showing the evaluation result of hydrogen storage performance of CPPIZ in Example 11;

FIG. 12 is a graph showing the evaluation result of hydrogen storage performance of THPEA in Example 12;

FIG. 13 is a graph showing the evaluation result of hydrogen storage performance of HQ in Example 13;

FIG. 14 is a graph showing the evaluation result of hydrogen storage performance of urea in Example 14;

FIG. 15 is a graph showing the evaluation result of hydrogen storage performance of AC in Example 15;

FIG. 16 is a graph showing the evaluation result of hydrogen storage performance of CD in Example 16;

FIG. 17 is a graph showing the evaluation result of hydrogen storage performance of GAM in Example 17;

FIG. 18 is a graph showing the evaluation result of hydrogen storage performance of DCA in Example 18;

FIG. 19 is a graph showing the evaluation result of hydrogen storage performance of cellulose in Example 19;

FIG. 20 is a graph showing the evaluation result of hydrogen storage performance of chitosan in Example 20;

FIG. 21 is a graph showing the evaluation result of hydrogen storage performance of TTP in Example 21;

FIG. 22 is a graph showing IR spectrum of a hydrogen clathrate (Crystal A) produced in Example 22;

FIG. 23 is a graph showing IR spectrum of a methanol clathrate (Crystal B) produced in Example 22;

FIG. 24 is a graph showing the IR spectrum of Fig. 22 and IR spectrum of Fig. 23 superposed to each other;

FIG. 25 is a graph showing TG-DTA detection curve of hydrogen clathrate (Cristalline A) prepared in Example 22.

FIG. 26 is a graph showing TG-DTA detection curve of methanol clathrate (Cristalline B) prepared in Example 22.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[Description of method for storing hydrogen]

[0019] Hereinafter, a preferred embodiment of the method of hydrogen storage of the present invention will be described in detail.

[0020] In the present invention, an organic compound used in hydrogen storage may be any one of organic compounds capable of storing hydrogen when it is in contact with hydrogen gas under pressurized condition, except organic compounds consisting of carbon atoms only. Other than that, there is no particular limitation on the organic compound used in hydrogen storage. The organic compound may contain metallic component and may not contain metallic component.

[0021] Among hydrogen molecular compounds, known as organic compounds forming hydrogen clathrates containing hydrogen molecules are host compounds of monomolecular type, multimolecular type, high-molecular type, and the like.

[0022] Examples of host compounds of monomolecular type include cyclodextrins, crown ethers, cryptands, cyclophanes, azacyclophanes, calixarenes, cyclotriveratrylenes, spherands, and cyclic oligopeptides. Examples of host compounds of multimolecular type include ureas, thioureas, deoxycholates, perhydrotriphenylenes, tri-o-thymotides, bianthryls, spirobifluorenes, cyclophosphazenes, monoalcohols, diols, acetylene alcohols, hydroxybenzophenones, phenols, bisphenols,

trisphenols, tetrakis phenol-base, polyphenols, naphthols, bis-naphthols, diphenylmehanols, carboxylic amides, thioamides, bixanthene, carboxylic acids, imidazoles, and hydroquinones. Examples of host compounds of high-molecular type include celluloses, starchs, chitins, chitosans, and polyvinyl alcohols, polymers of polyethylene glycol arm type of which core is 1,1,2,2-tetrakis phenyl ethane, and polymers of polyethylene glycol arm type of which core is $\alpha,\alpha,\alpha',\alpha'$-tetrakis phenyl xylene.

[0023] Other than those, examples of host compounds may also include organic phosphorous compounds and organic silicon compounds.

[0024] Further, some of organic metallic compounds have characteristics functioning as host compound and include, for examples, organic aluminum compounds, organic titanium compounds, organic boron compounds, organic zinc compounds, organic indium compounds, organic gallium compounds, organic tellurium compounds, organic tin compounds, organic zirconium compounds, and organic magnesium compounds. Further, a metallic salt of organic carboxylic acid or an organic metallic complex may be employed. However, organic metallic compounds are not limited to those listed above.

[0025] Among the above host compounds, host compounds of multimolecular type of which enclosure capacity is hardly influenced by the size of molecules of guest compound are preferable.

[0026] Concrete examples of host compounds of multimolecular type are urea,
1,1,6,6-tetraphenyl-2,4-hexadiyn-1,6-diol,
1,1-bis(2,4-dimethylphenyl)-2-propyn-1-ol,

1,1,4,4-tetraphenyl-2-butyne-1,4-diol, 1,1,6,6-tetrakis(2,4-dimethylphenyl)-2,4-hexadiyn-1,6-diol, 9,10-diphyenyl-9,10-dihydroanthracene-9,10-diol, 9,10-bis(4-methylphenyl)-9,10-dihydroanthracene-9,10-diol, 1,1,2,2-tetraphenylethane-1,2-diol, 4-methoxyphenol, 2,4-dihydroxybenzophenone, 4,4′-dihydroxybenzophenone, 2,2′-dihydroxybenzophenone, 2,2′,4,4′-tetrahydroxybenzophenone, 1,1-bis(4-hydroxyphenyl)cyclohexane, 4,4′-sulfonyl bisphenol, 2,2′-methylene bis(4-methyl-6-t-buthylphenol), 4,4′-ethylidene bisphenol, 4,4′-thiobis(3-methyl-6-t-butylphenol), 1,1,3-tris(2-methyl-4-hydroxy-5-t-buthylphenyl)butane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethylene, 1,1,2,2-tetrakis(3-mehyl-4-hydroxyphenyl)ethane, 1,1,2,2-tetrakis(3-fluoro-4-hydroxyphenyl)ethane, α,α,α′,α′-tetrakis(4-hydroxyphenyl)-p-xylene, tetrakis(p-methoxyphenyl)ethylene, 3,6,3′,6′-tetramethoxy-9,9′-bi-9H-xanthene, 3,6,3′,6′-tetra acetoxy-9,9′-bi-9H-xanthene, 3,6,3′,6′-tetrahyroxy-9,9′-bi-9H-xanthene, gallic acid, methyl gallate, catechin, bis-β-naphthol, α,α,α′,α′-tetraphenyl-1,1′-biphenyl-2,2′-dimethanol, bis-dicyclohexylamide diphenirate, bis-dicyclohexylamide fumarate, cholic acid, deoxycholic acid, 1,1,2,2-tetraphenylethane, tetrakis(p-iodophenyl)ethylene, 9,9'-bianthryl, 1,1,2,2-tetrakis(4-carboxyphenyl)ethane, 1,1,2,2-tetrakis(3-carboxyphenyl)ethane, acetylene dicarboxyl acid, 2,4,5-triphenyl imidazole,

1,2,4,5-tetraphenyl imidazole, 2-phenyl phenanthro[9,10-d]imidazole, 2-(o-cyanophenyl)phenanthro[9,10-d]imidazole, 2-(m-cyanophenyl)phenanthro[9,10-d]imidazole, 2-(p-cyanophenyl)phenanthro[9,10-d]imidazole, hydroquinone, 2-t-buthyl hydroquinone, 2,5-di-t-buthyl hydroquinone, and 2,5-bis(2,4-dimethylphenyl)hydroquinone. Among these, especially preferably employed host compounds in view of enclosure capacity are phenol-based host compounds such as 1,1-bis(4-hydroxyphenyl)cyclohexane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, and 1,1,2,2-tetrakis(4-hydroxyphenyl)ethylene; aromatic host compounds such as tetrakis(p-methoxyphenyl)ethylene, tetrakis(p-iodophenyl)ethylene, 9,9'-bianthryl and 1,1,2,2-tetraphenylethane; amide-based host compounds such as bis(dicyclohexylamide)diphenirate and bis-dicyclohexylamide fumarate; alcohol-based host compounds such as α,α,α′,α′-tetraphenyl-1,1′-biphenyl-2,2′-dimethanol and 1,1,6,6-tetraphenyl-2,4-hexadiyn-1,6-diol; and imidazole-based host compounds such as 2-(m-cyanophenyl)phenanthro[9,10-d]imidazole; and organic phosphorous compound such as tri-m-trylphosphine.

[0027] These host compounds may be used alone or may be used in combination with one or more among the others.

[0028] It is particularly preferable that the organic compound to be used is solid in powder form in view of contact efficiency with hydrogen gas. However, the organic compound is not limited thereto and may be in granular form or in aggregated form and also may be in crystalloid form or in amorphous form. Further, the organic compound may be liquid

or gaseous. When the organic compound is solid in powder form, there is no particular limitation on it particle diameter, but normally the particle diameter is preferably about 1 mm or less.

[0029] The organic compound may be used to be a complex material containing the organic compound supported on a porous carrier or support. In this case, examples of the porous carrier supporting the organic compound include, but not limited to, silicas, zeolites, or activated carbons, alternatively, interlaminar compounds such as a clay mineral or montmorillonite. The complex material containing the organic compound can be manufactured by, for example, a method of dissolving the organic compound in a solvent capable of dissolving the organic compound, impregnating the porous carrier with the organic compound solution, drying the solvent, and decompressing and drying them. There is no limitation on the amount of the organic material supported on the porous carrier. However, the amount of the organic material is normally in a range from 10 to 80 % by weight relative to the porous carrier.

[0030] It is known that the aforementioned host compound such as 1,1-bis(4-hydroxyphenyl)cyclohexane or bis(dicyclohexylamide)diphenirate receives various guest molecules to form a crystal clathrate. It is also known that a clathrate is formed by bringing the host compound in contact with a guest compound (may be solid, liquid, or gaseous). In the present invention, the gaseous molecular of hydrogen gas is brought in contact with the organic compound as the host compound in the pressurized state so that hydrogen molecules are enclosed in the clathrate, thereby stably storing hydrogen.

[0031] As for the pressurizing condition under which hydrogen gas and solid organic compound are in contact with each other,

higher pressure is preferable because larger storage amount and higher storage speed of hydrogen are possible. On the other hand, the pressurizer should be expensive and, in addition, it should be required to satisfy the regulations of High Pressure Gas Safety Law. Normally, the pressurizing condition is higher than the 1.0×10^{-10} MPa and is preferably in a range from 1.0×10^{-10} MPa to 200 MPa. It is more preferably higher than the ambient pressure by 0.1 MPa to 70 MPa, actually especially by 0.1 to 0.9 MPa.

[0032] As the contact time is longer, the hydrogen storage rate can be increased. In view of working efficiency, the contact time is preferably in a range from 0.01 to 24 hours.

[0033] The hydrogen gas to be brought in contact with the organic compound is preferably high-purity hydrogen. However, as will be described below, it may be a mixed gas of hydrogen gas and other gas in case of using host compound having selective enclosure capacity of hydrogen.

[0034] A hydrogen clathrate obtained as mentioned above is a hydrogen clathrate normally having hydrogen molecules from 0.1 to 20 moles relative to 1 mole of the host compound, but somewhat depends on the kind of used host compound and the contact condition with hydrogen.

[0035] Such a hydrogen clathrate as mentioned above can stably enclose hydrogen for a long period of time at ordinary temperature and ambient pressure. Moreover, the hydrogen clathrate is light as compared to hydrogen storage alloy and thus has excellent handling property. In addition, since the hydrogen clathrate is solid, the hydrogen clathrate can be in powder form having particle diameter of 1 mm or less and thus can be easily stored and transported in a container made of glass,

metal, or plastic.

[0036] According to the method of the present invention, in case that hydrogen is stored in the pressurized state, the hydrogen can be taken off from the stored state by depressurizing or heating. The hydrogen can be taken off from the stored state also by heating and depressurizing at the same time.

[0037] Particularly, hydrogen can be emitted from the hydrogen clathrate by heating the hydrogen clathrate to a temperature in a range from 30 °C to 200 °C, particularly in a range from 40 °C to 100 °C under ambient pressure or a reduced pressure lower than the ambient pressure by 1.0×10^{-2} MPa to 1.0×10^{-5} MPa, but the condition somewhat depends on the kind of the host compound. Therefore, hydrogen can be easily emitted from the hydrogen clathrate and used for various applications.

[0038] The host compound after the hydrogen is emitted from the hydrogen clathrate still has the selective enclosure capacity of hydrogen so that it is effectively reusable.

[0039] The method for storing hydrogen of the present invention will be described in detail with reference to Examples. In Examples 1-19, evaluation test of hydrogen storage property was conducted according to the following method.

<Evaluation test of hydrogen storage property>

1) Evaluation Method

[0040] According to Japan Industrial Standard (JIS) H-7201 entitled "Method of termining the PCT relations of hydrogen absorbing alloys", the measurement was conducted by using a hydrogen emission evaluation equipment available from LESCA CORPORATION.

2) Specimen

[0041] A test tube having volume of 25ml was filled with

specimen of about 0.1g to 1g, and the weight of the specimen was measured precisely. The test tube was then filled with helium gas, and was measured its airtightness for more than 12 hours. It was found to have enough airtightness. After that, the inner volume of the tube other than the specimen was detected.

3) Pretreatment

[0042] The specimen was heated to 50 °C and was vacuumed and depressurized for 3 hours by a rotary pump.

4) Evaluation Condition

[0043] The test tube filled with the specimen was retained in a temperature-controlled bath at 25 °C during the test. Hydrogen gas was introduced with changing the pressure to balance the pressure. When the pressure was balanced, the storage amount was measured. The measurement was conducted under such a condition that the retention time at each balanced pressure was 1 hour or 8 hours.

EXAMPLE 1

[0044] 0.5602g of 1,1-bis(4-hydroxyphenyl)cyclohexane (hereinafter, referred to as "BHC") in solid power state was prepared as a specimen. The specimen was evaluated according to the aforementioned test method under such a condition that the retention time at each pressure was 1 hour. The relation between the balanced pressure and the hydrogen storage rate was shown in Table 1 and Fig. 1.

Table 1

Evaluation Results of Hydrogen Storage Capacity of BHC

(25°C; Retention time at each pressure: 1 hour)

Balanced Pressure (MPa)	Hydrogen Storage Rate (wt%)
0.00001	0
0.28512	2.72E-05
2.56316	5.06E-04
3.58284	1.70E-02
4.74355	4.69E-02
4.37443	5.58E-02
3.59104	6.71E-02
2.69834	7.58E-02
1.54989	7.46E-02
0.85812	7.30E-02
0.31544	6.83E-02

[0045] From the results shown in Table 1 and Fig. 1, it was found that the hydrogen storage rate was increased as the hydrogen pressure was increased. Even when the pressure was reduced from near 5 MPa, the storage rate is not lowered. From this, it was found that the hydrogen storage is achieved not only by physical absorption. This is attributed to the fact that hydrogen molecules are enclosed into the solid BHC so as to form hydrogen clathrate.

[0046] We confirmed that stored hydrogen can be emitted under condition of 50 °C and the ambient pressure or under condition of a reduced pressure (0.005 MPa).

EXAMPLE 2

[0047] 0.2361g of the BHC in solid power state, used in Example 1, of which hydrogen was emitted was prepared as a specimen. The specimen was evaluated according to the aforementioned test method under such a condition that the retention time at each pressure was 8 hour. The relation between the balanced pressure

and the hydrogen storage rate was shown in Table 2 and Fig. 2.

Table 2

Evaluation Results of Hydrogen Enclosure Capacity of BHC (25°C; Retention time at each pressure: 8 hour)

Balanced Pressure (MPa)	Hydrogen Storage Rate (wt%)
0.00001	0
0.26998	8.99E-03
0.75076	2.43E-02
1.54598	4.25E-02
2.48468	7.11E-02
3.42314	1.08E-01
4.40393	1.39E-01
5.98982	2.53E-01
8.9985	2.86E-01
7.7586	3.41E-01
6.08094	3.93E-01
4.8332	3.57E-01
3.70449	3.72E-01
2.47191	3.99E-01
1.58845	4.09E-01
0.8876	4.11E-01
0.33885	4.02E-01

[0048] From the results shown in Table 2 and Fig. 2, it was found that the hydrogen storage rate in case that the retention time was 8 hours was increased as compared to the case that the retention time was 1 hour.

[0049] We confirmed that stored hydrogen can be emitted under condition of 50 °C and the ambient pressure or under condition of a reduced pressure (0.005 MPa). It is found from this that the method for storing hydrogen of the present invention enables repetition of enclosure and emission of hydrogen.

EXAMPLE 3

[0050] 0.5897g of 9,9'-bianthryl (hereinafter, referred to as "BA") in solid power state was evaluated according to the aforementioned test method under such a condition that the retention time at each pressure was 1 hour. The relation between the balanced pressure and the hydrogen storage rate was shown in Table 3 and Fig. 3.

Table 3

Evaluation Results of Hydrogen Storage Capacity of BA (25°C; Retention time at each pressure: 1 hour)

Balanced Pressure (MPa)	Hydrogen Storage Rate (wt%)
0.00001	0
0.29628	2.51E-03
0.76323	1.99E-03
1.56556	1.34E-03
2.4644	5.50E-05
3.44561	4.59E-04
4.42035	7.60E-03
7.83902	2.44E-02
6.06874	3.10E-02
4.80743	3.93E-02
3.72473	4.50E-02
2.67821	4.41E-02
1.65635	4.55E-02
0.97333	4.55E-02
0.4255	4.32E-02
0.15678	4.48E-02

[0051] From the results shown in Table 3 and Fig. 3, it was found that the hydrogen storage rate was increased as the hydrogen pressure was increased. Even when the pressure was reduced from near 8 MPa, the storage rate is not lowered. From this, it was found that the hydrogen storage is achieved not only by physical absorption. This is attributed to the fact that hydrogen molecules are enclosed into the solid BA so as to form hydrogen clathrate.

[0052] We confirmed that stored hydrogen can be emitted under condition of 50 °C and the ambient pressure or under condition of a reduced pressure (0.005 MPa).

EXAMPLE 4

[0053] 0.523g of 1,1,2,2-tetrakis(4-hydroxyphenyl)ethylene (hereinafter, referred to as "THPEY") in solid power state was evaluated according to the aforementioned test method under such a condition that the retention time at each pressure was 1 hour. The relation between the balanced pressure and the hydrogen storage rate was shown in Table 4 and Fig. 4.

Table 4

Evaluation Results of Hydrogen Storage Capacity of THPEY (25°C; Retention time at each pressure: 1 hour)

Balanced Pressure (MPa)	Hydrogen Storage Rate (wt%)
0.00001	0
0.2859	2.86E-03
0.75946	2.51E-03
1.56681	4.67E-03
2.48916	7.66E-03
3.42975	1.87E-02
4.40985	2.89E-02
7.91528	4.98E-02
6.1531	5.87E-02
4.86329	6.50E-02
3.73287	7.12E-02
2.78108	7.30E-02
1.68593	7.43E-02
0.91052	7.20E-02
0.39254	7.04E-02
0.05198	6.90E-02

[0054] From the results shown in Table 4 and Fig. 4, it was found that the hydrogen storage rate was increased as the hydrogen pressure was increased. Even when the pressure was

reduced from near 8 MPa, the storage rate is not lowered. From this, it was found that the hydrogen storage is achieved not only by physical absorption. This is attributed to the fact that hydrogen molecules are enclosed into the solid THPEY so as to form hydrogen clathrate.

[0055] We confirmed that stored hydrogen can be emitted under condition of 50 °C and the ambient pressure or under condition of a reduced pressure (0.005 MPa).

EXAMPLE 5

[0056] 0.510g of tetrakis(p-methoxyphenyl)ethylene (hereinafter, referred to as "TMPE") in solid power state was evaluated according to the aforementioned test method under such a condition that the retention time at each pressure was 1 hour. The relation between the balanced pressure and the hydrogen storage rate was shown in Table 5 and Fig. 5.

Table 5

Evaluation Results of Hydrogen Storage Capacity of TMPE

(25°C; Retention time at each pressure: 1 hour)

Balanced Pressure (MPa)	Hydrogen Storage Rate (wt%)
0.00001	0
0.34802	2.00E-03
0.77991	1.34E-04
1.556	8.87E-04
2.47892	1.06E-03
3.43927	8.98E-04
4.41114	2.49E-04
7.82444	1.43E-02
6.03258	2.48E-02
4.77365	3.11E-02
3.66555	3.66E-02
2.6391	4.19E-02
1.62859	4.20E-02
0.93906	4.13E-02
0.41354	3.89E-02
0.15272	3.90E-02

[0057] From the results shown in Table 5 and Fig. 5, it was found that the hydrogen storage rate was increased as the hydrogen pressure was increased. Even when the pressure was reduced from near 8 MPa, the storage rate is not lowered. From this, it was found that the hydrogen storage is achieved not only by physical absorption. This is attributed to the fact that hydrogen molecules are enclosed into the solid TMPE so as to form hydrogen clathrate.

[0058] We confirmed that stored hydrogen can be emitted under condition of 50 °C and the ambient pressure or under condition of a reduced pressure (0.005 MPa).

EXAMPLE 6

[0059] 0.615g of 1,1,2,2-tetraphenylethane (hereinafter, referred to as "TPE") in solid power state was evaluated

according to the aforementioned test method under such a condition that the retention time at each pressure was 1 hour. The relation between the balanced pressure and the hydrogen storage rate was shown in Table 6 and Fig. 6.

Table 6

Evaluation Results of Hydrogen Storage Capacity of TPE (25°C; Retention time at each pressure: 1 hour)

Balanced Pressure (MPa)	Hydrogen Storage Rate (wt%)
0.00001	0
0.29124	2.08E-03
0.7583	3.31E-03
1.55817	9.53E-03
2.49921	1.79E-02
3.47931	3.37E-02
4.45467	4.56E-02
7.85865	7.99E-02
6.09663	7.89E-02
4.80934	7.35E-02
3.67186	7.14E-02
2.64523	6.48E-02
1.63782	5.95E-02
0.95366	5.56E-02
0.41393	4.98E-02
0.15164	4.87E-02

[0060] From the results shown in Table 6 and Fig. 6, it was found that the hydrogen storage rate was increased as the hydrogen pressure was increased. Even when the pressure was reduced from near 8 MPa, the storage rate is not lowered. From this, it was found that the hydrogen storage is achieved not only by physical absorption. This is attributed to the fact that hydrogen molecules are enclosed into the solid TPE so as to form hydrogen clathrate.

[0061] We confirmed that stored hydrogen can be emitted under condition of 50 °C and the ambient pressure or under condition

of a reduced pressure (0.005 MPa).

EXAMPLE 7

[0062] 0.547g of bis-dicyclohexylamide diphenirate (hereinafter, referred to as "DBDCA") in solid power state was evaluated according to the aforementioned test method under such a condition that the retention time at each pressure was 1 hour. The relation between the balanced pressure and the hydrogen storage rate was shown in Table 7 and Fig. 7.

Table 7

Evaluation Results of Hydrogen Storage Capacity of DBDCA (25°C; Retention time at each pressure: 1 hour)

Balanced Pressure (MPa)	Hydrogen Storage Rate(wt%)
0.00001	0
0.26798	2.60E-03
0.61094	5.37E-03
1.5056	1.02E-02
2.50882	1.88E-02
3.46749	3.28E-02
4.50091	4.32E-02
7.98069	7.74E-02
6.12568	8.49E-02
4.82424	8.90E-02
3.71524	8.71E-02
2.68839	8.50E-02
1.67032	7.75E-02
0.88976	7.14E-02
0.39007	6.94E-02

[0063] From the results shown in Table 7 and Fig. 7, it was found that the hydrogen storage rate was increased as the hydrogen pressure was increased. Even when the pressure was reduced from near 8 MPa, the storage rate is not lowered. From this, it was found that the hydrogen storage is achieved not only by physical absorption. This is attributed to the fact that

hydrogen molecules are enclosed into the solid DBDCA so as to form hydrogen clathrate.

[0064] We confirmed that stored hydrogen can be emitted under condition of 50 °C and the ambient pressure or under condition of a reduced pressure (0.005 MPa).

EXAMPLE 8

[0065] 0.6442g of bis-dicyclohexylamide fumarate (hereinafter, referred to as "FBDCA") in solid power state was evaluated according to the aforementioned test method under such a condition that the retention time at each pressure was 1 hour. The relation between the balanced pressure and the hydrogen storage rate was shown in Table 8 and Fig. 8.

Table 8

Evaluation Results of Hydrogen Storage Capacity of FBDCA (25°C; Retention time at each pressure: 1 hour)

Balanced Pressure (MPa)	Hydrogen Storage Rate (wt%)
0.00001	0
0.27639	0.00E+00
0.76462	0.00E+00
1.58534	0.00E+00
2.5095	3.33E-04
3.49362	5.11E-03
4.50578	8.88E-03
7.91723	2.13E-02
6.11502	3.74E-02
4.80353	5.04E-02
3.69892	5.68E-02
2.66783	6.15E-02
1.66457	6.39E-02
0.86552	6.55E-02
0.38038	6.58E-02
0.20061	6.71E-02
0.13619	6.58E-02

[0066] From the results shown in Table 8 and Fig. 8, it was

found that the hydrogen storage rate was increased as the hydrogen pressure was increased. Even when the pressure was reduced from near 8 MPa, the storage rate is not lowered. From this, it was found that the hydrogen storage is achieved not only by physical absorption. This is attributed to the fact that hydrogen molecules are enclosed into the solid FBDCA so as to form hydrogen clathrate.

[0067] We confirmed that stored hydrogen can be emitted under condition of 50 °C and the ambient pressure or under condition of a reduced pressure (0.005 MPa).

EXAMPLE 9

[0068] 0.6456g of α,α,α′,α′-tetraphenyl-1,1′-biphenyl-2,2′-dimethanol (hereinafter, referred to as "TPBDM") in solid power state was evaluated according to the aforementioned test method under such a condition that the retention time at each pressure was 1 hour. The relation between the balanced pressure and the hydrogen storage rate was shown in Table 9 and Fig. 9.

Table 9

Evaluation Results of Hydrogen Storage Capacity of TPBDM

(25°C; Retention time at each pressure: 1 hour)

Balanced Pressure (MPa)	Hydrogen Storage Rate (wt%)
0.00001	0
0.27325	3.86E-03
0.76318	5.86E-03
1.57435	7.25E-03
2.52014	9.34E-03
3.51926	1.45E-02
4.48755	1.76E-02
7.94765	3.55E-02
6.14546	4.55E-02
4.82544	5.52E-02
3.72633	5.88E-02
2.68608	6.06E-02
1.66871	5.98E-02
1.3472	6.10E-02
0.56019	5.90E-02
0.26901	5.95E-02
0.16055	5.96E-02

[0069] From the results shown in Table 9 and Fig. 9, it was found that the hydrogen storage rate was increased as the hydrogen pressure was increased. Even when the pressure was reduced from near 8 MPa, the storage rate is not lowered. From this, it was found that the hydrogen storage is achieved not only by physical absorption. This is attributed to the fact that hydrogen molecules are enclosed into the solid TPBDM so as to form hydrogen clathrate.

[0070] We confirmed that stored hydrogen can be emitted under condition of 50 °C and the ambient pressure or under condition of a reduced pressure (0.005 MPa).

EXAMPLE 10

[0071] 0.631g of 1,1,6,6-tetraphenyl-2,4-hexadiyn-1,6-diol (hereinafter, referred to as "TPHDD") in solid power state was evaluated according to the aforementioned test method under such a condition that the retention time at each pressure was 1 hour. The relation between the balanced pressure and the hydrogen storage rate was shown in Table 10 and Fig. 10.

Table 10

Evaluation Results of Hydrogen Storage Capacity of TPHDD (25°C; Retention time at each pressure: 1 hour)

Balanced Pressure (MPa)	Hydrogen Storage Rate (wt%)
0.00001	0
0.2846	3.86E-03
0.76446	1.15E-03
1.56681	4.67E-03
2.49036	7.66E-03
3.44995	1.87E-02
4.48085	2.89E-02
7.92517	4.98E-02
6.15209	5.87E-02
4.85724	6.50E-02
3.73289	7.12E-02
2.73198	7.30E-02
1.68694	7.43E-02
0.90154	7.20E-02
0.39853	7.04E-02
0.21299	6.90E-02
0.14233	6.85E-02
0.05198	6.90E-02

[0072] From the results shown in Table 10 and Fig. 10, it was found that the hydrogen storage rate was increased as the hydrogen pressure was increased. Even when the pressure was reduced from near 8 MPa, the storage rate is not lowered. From this, it was found that the hydrogen storage is achieved not only by physical absorption. This is attributed to the fact that

hydrogen molecules are enclosed into the solid TPHDD so as to form hydrogen clathrate.

[0073] We confirmed that stored hydrogen can be emitted under condition of 50 °C and the ambient pressure or under condition of a reduced pressure (0.005 MPa).

EXAMPLE 11

[0074] 0.2256g of 2-(m-cyanophenyl)phenanthro[9,10-d]imidazole (hereinafter, referred to as "CPPZZ") in solid power state was evaluated according to the aforementioned test method under such a condition that the retention time at each pressure was 1 hour. The relation between the balanced pressure and the hydrogen storage rate was shown in Table 11 and Fig. 11.

Table 11

Evaluation Results of Hydrogen Storage Capacity of CPPIZ

(25°C; Retention time at each pressure: 1 hour)

Balanced Pressure (MPa)	Hydrogen Storage Rate (wt%)
0.00001	0
0.27501	3.67E-03
0.74744	6.10E-03
1.55025	1.05E-02
2.48037	1.42E-02
3.42067	1.95E-02
4.42905	3.54E-02
7.823	4.91E-02
6.09215	8.70E-02
4.83169	9.98E-02
3.70401	1.14E-01
2.66689	1.16E-01
1.67919	1.14E-01
0.92012	1.08E-01
0.41564	9.85E-02
0.22111	1.01E-01
0.41659	1.01E-01
0.05505	9.86E-02

[0075] From the results shown in Table 11 and Fig. 11, it was found that the hydrogen storage rate was increased as the hydrogen pressure was increased. Even when the pressure was reduced from near 8 MPa, the storage rate is not lowered. From this, it was found that the hydrogen storage is achieved not only by physical absorption. This is attributed to the fact that hydrogen molecules are enclosed into the solid CPPIZ so as to form hydrogen clathrate.

[0076] We confirmed that stored hydrogen can be emitted under condition of 50 °C and the ambient pressure or under condition of a reduced pressure (0.005 MPa).

EXAMPLE 12

[0077] 0.5188g of 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane (hereinafter, referred to as "THPEA") in solid power state was evaluated according to the aforementioned test method under such a condition that the retention time at each pressure was 1 hour. The relation between the balanced pressure and the hydrogen storage rate was shown in Table 12 and Fig. 12.

Table 12

Evaluation Results of Hydrogen Storage Capacity of THPEA (25°C; Retention time at each pressure: 1 hour)

Balanced Pressure (MPa)	Hydrogen Storage Rate (wt%)
0.00001	0
0.29865	3.93E-03
0.68963	4.98E-03
1.38148	3.34E-03
2.16169	9.01E-04
3.59962	2.72E-03
4.8627	7.64E-03
8.21891	2.68E-02
6.4096	4.14E-02
5.14432	3.18E-02
3.55335	3.10E-02
2.44797	2.82E-02
1.50235	2.45E-02
0.85956	2.20E-02
0.38532	2.11E-02
0.14243	1.81E-02

[0078] From the results shown in Table 12 and Fig. 12, it was found that the hydrogen storage rate was increased as the hydrogen pressure was increased. Even when the pressure was reduced from near 8 MPa, the storage rate is not lowered. From this, it was found that the hydrogen storage is achieved not only by physical absorption. This is attributed to the fact that hydrogen molecules are enclosed into the solid THPEA so as to form hydrogen clathrate.

[0079] We confirmed that stored hydrogen can be emitted under condition of 50 °C and the ambient pressure or under condition of a reduced pressure (0.005 MPa).

EXAMPLE 13

[0080] 0.7029g of hydroquinone (hereinafter, referred to as "HQ") in solid power state was evaluated according to the aforementioned test method under such a condition that the retention time at each pressure was 1 hour. The relation between the balanced pressure and the hydrogen storage rate was shown in Table 13 and Fig. 13.

Table 13

Evaluation Results of Hydrogen Storage Capacity of HQ

(25°C; Retention time at each pressure: 1 hour)

Balanced Pressure (MPa)	Hydrogen Storage Rate (wt%)
0.00001	0
0.34576	5.92E-03
0.77692	1.02E-02
1.55369	1.99E-02
2.48608	2.69E-02
3.47638	3.21E-02
4.44271	3.94E-02
7.84616	8.34E-02
6.07125	7.89E-02
4.79427	7.32E-02
3.69405	6.47E-02
2.65721	5.42E-02
1.64583	4.88E-02
0.78016	3.64E-02
0.38000	3.05E-02
0.13936	2.76E-02

[0081] From the results shown in Table 13 and Fig. 13, it was found that the hydrogen storage rate was increased as the hydrogen pressure was increased.

[0082] We confirmed that stored hydrogen can be emitted under condition of 50 °C and the ambient pressure or under condition of a reduced pressure (0.005 MPa).

EXAMPLE 14

[0083] 0.3482g of urea in solid power state was evaluated according to the aforementioned test method under such a condition that the retention time at each pressure was 1 hour. The relation between the balanced pressure and the hydrogen storage rate was shown in Table 14 and Fig. 14.

Table 14

Evaluation Results of Hydrogen Storage Capacity of urea (25°C; Retention time at each pressure: 1 hour)

Balanced Pressure (MPa)	Hydrogen Storage Rate (wt%)
0.00001	0
0.26619	1.09E-03
0.79056	1.22E-03
1.584	3.11E-03
2.51682	2.82E-03
3.49309	1.78E-04
4.46605	1.51E-02
7.91202	3.92E-02
6.08862	5.12E-02
4.81388	5.47E-02
3.70222	5.38E-02
2.64015	4.92E-02
1.62255	3.83E-02
0.96213	3.32E-02
0.40202	3.16E-02
0.1442	2.95E-02

[0084] From the results shown in Table 14 and Fig. 14, it was found that the hydrogen storage rate was increased as the hydrogen pressure was increased. Even when the pressure was reduced from near 8 MPa, the storage rate is not lowered. From

this, it was found that the hydrogen storage is achieved not only by physical absorption. This is attributed to the fact that hydrogen molecules are enclosed into the solid urea so as to form hydrogen clathrate.

[0085] We confirmed that stored hydrogen can be emitted under condition of 50 °C and the ambient pressure or under condition of a reduced pressure (0.005 MPa).

EXAMPLE 15

[0086] 0.888g of acetylene dicarboxyl acid (hereinafter, referred to as "AC") in solid power state was evaluated according to the aforementioned test method under such a condition that the retention time at each pressure was 1 hour. The relation between the balanced pressure and the hydrogen storage rate was shown in Table 15 and Fig. 15.

Table 15

Evaluation Results of Hydrogen Storage Capacity of AC

(25°C; Retention time at each pressure: 1 hour)

Balanced Pressure (MPa)	Hydrogen Storage Rate (wt%)
0.00001	0
0.27146	3.40E-03
0.74369	6.02E-03
1.5659	1.02E-02
2.50809	1.30E-02
3.47403	1.81E-02
4.45074	1.42E-02
7.88744	2.29E-02
6.11056	2.47E-02
4.78659	2.57E-02
3.69364	2.48E-02
2.65705	2.40E-02
1.63543	2.09E-02
0.86718	1.83E-02
0.37335	1.68E-02
0.1354	1.68E-02

[0087] From the results shown in Table 15 and Fig. 15, it was found that the hydrogen storage rate was increased as the hydrogen pressure was increased. Even when the pressure was reduced from near 8 MPa, the storage rate is not lowered. From this, it was found that the hydrogen storage is achieved not only by physical absorption. This is attributed to the fact that hydrogen molecules are enclosed into the solid AC so as to form hydrogen clathrate.

[0088] We confirmed that stored hydrogen can be emitted under condition of 50 °C and the ambient pressure or under condition of a reduced pressure (0.005 MPa).

EXAMPLE 16

[0089] 0.8967g of β-cyclodextrin (hereinafter, referred to as "CD") in solid power state was evaluated according to the aforementioned test method under such a condition that the retention time at each pressure was 1 hour. The relation between the balanced pressure and the hydrogen storage rate was shown in Table 16 and Fig. 16.

Table 16

Evaluation Results of Hydrogen Storage Capacity of CD

(25°C; Retention time at each pressure: 1 hour)

Balanced Pressure(MPa)	Hydrogen Storage Rate (wt%)
0.00001	0
0.29994	2.20E-03
0.63	1.30E-03
1.59541	2.29E-04
2.61668	5.74E-03
3.47134	1.37E-02
4.44424	2.14E-02
7.87665	5.17E-02
6.17737	4.61E-02
4.90025	3.92E-02
3.72096	3.15E-02
2.7198	2.45E-02
1.5438	1.53E-02
0.85297	9.75E-03
0.37524	5.25E-03
0.13649	2.22E-03

[0090] From the results shown in Table 16 and Fig. 16, it was found that the hydrogen storage rate was increased as the hydrogen pressure was increased.

EXAMPLE 17

[0091] 0.7383g of methyl gallate (hereinafter, referred to as "GAM") in solid power state was evaluated according to the aforementioned test method under such a condition that the retention time at each pressure was 1 hour. The relation between the balanced pressure and the hydrogen storage rate was shown in Table 17 and Fig. 17.

Table 17

Evaluation Results of Hydrogen Storage Capacity of GAM

(25°C; Retention time at each pressure: 1 hour)

Balanced Pressure (MPa)	Hydrogen Storage Rate (wt%)
0.00001	0
0.29993	2.27E-03
0.70041	2.40E-03
1.9847	2.90E-03
2.7857	7.70E-03
3.53863	9.03E-03
4.6868	1.21E-02
7.98167	3.17E-02
6.36749	3.31E-02
5.03659	3.48E-02
3.9262	3.26E-02
2.59506	2.61E-02
1.54629	2.32E-02
0.86813	2.07E-02
0.38689	1.90E-02
0.14084	1.96E-02

[0092] From the results shown in Table 17 and Fig. 17, it was found that the hydrogen storage rate was increased as the hydrogen pressure was increased. Even when the pressure was reduced from near 8 MPa, the storage rate is not lowered. From this, it was found that the hydrogen storage is achieved not only by physical absorption. This is attributed to the fact that hydrogen molecules are enclosed into the solid GAM so as to form hydrogen clathrate.

[0093] We confirmed that stored hydrogen can be emitted under condition of 50 °C and the ambient pressure or under condition of a reduced pressure (0.005 MPa).

EXAMPLE 18

[0094] 0.7411g of deocycholic acid (hereinafter, referred to

as "DCA") in solid power state was evaluated according to the aforementioned test method under such a condition that the retention time at each pressure was 1 hour. The relation between the balanced pressure and the hydrogen storage rate was shown in Table 18 and Fig. 18.

Table 18

Evaluation Results of Hydrogen Storage Capacity of DCA (25°C; Retention time at each pressure: 1 hour)

Balanced Pressure (MPa)	Hydrogen Storage Rate (wt%)
0.00001	0
0.30282	3.91E-03
0.69569	3.72E-03
1.41085	3.74E-03
2.54758	3.92E-03
3.62008	7.68E-03
4.63304	1.19E-02
7.96485	1.80E-02
6.2381	1.80E-02
4.98709	2.04E-02
3.89659	1.90E-02
2.56303	1.70E-02
1.52619	1.45E-02
0.85848	1.26E-02
0.38068	1.09E-02
0.13748	1.08E-02

[0095] From the results shown in Table 18 and Fig. 18, it was found that the hydrogen storage rate was increased as the hydrogen pressure was increased. Even when the pressure was reduced from near 8 MPa, the storage rate is not lowered. From this, it was found that the hydrogen storage is achieved not only by physical absorption. This is attributed to the fact that hydrogen molecules are enclosed into the solid DCA so as to form hydrogen clathrate.

[0096] We confirmed that stored hydrogen can be emitted under

condition of 50 °C and the ambient pressure or under condition of a reduced pressure (0.005 MPa).

EXAMPLE 19

[0097] 0.657g of cellulose in solid power state was evaluated according to the aforementioned test method under such a condition that the retention time at each pressure was 1 hour. The relation between the balanced pressure and the hydrogen storage rate was shown in Table 19 and Fig. 19.

Table 19

Evaluation Results of Hydrogen Storage Capacity of cellulose (25°C; Retention time at each pressure: 1 hour)

Balanced Pressure (MPa)	Hydrogen Storage Rate (wt%)
0.00001	0
0.29382	3.44E-03
1.75806	6.91E-03
1.78015	8.20E-03
2.33393	9.45E-03
3.67005	1.60E-02
4.88507	1.69E-02
8.25992	2.46E-02
6.49236	2.78E-02
5.18519	3.48E-02
3.57395	3.27E-02
2.44579	2.89E-02
2.50406	3.13E-02
1.23267	2.62E-02
0.52372	2.29E-02
0.19309	2.11E-02

[0098] From the results shown in Table 19 and Fig. 19, it was found that the hydrogen storage rate was increased as the hydrogen pressure was increased. Even when the pressure was reduced from near 8 MPa, the storage rate is not lowered. From

this, it was found that the hydrogen storage is achieved not only by physical absorption. This is attributed to the fact that hydrogen molecules are enclosed into the solid cellulose so as to form hydrogen clathrate.

[0099] We confirmed that stored hydrogen can be emitted under condition of 50 °C and the ambient pressure or under condition of a reduced pressure (0.005 MPa).

EXAMPLE 20

[0100] 0.6725g of chitosan in solid power state was evaluated according to the aforementioned test method under such a condition that the retention time at each pressure was 1 hour. The relation between the balanced pressure and the hydrogen storage rate was shown in Table 20 and Fig. 20.

Table 20

Evaluation Results of Hydrogen Storage Capacity of chitosan (25°C; Retention time at each pressure: 1 hour)

Balanced Pressure (MPa)	Hydrogen Storage Rate (wt%)
0.00001	0
0.30279	3.44E-03
0.69235	2.12E-03
2.15133	4.39E-03
2.97406	1.25E-02
3.91867	1.65E-02
4.9564	2.57E-02
8.17041	5.08E-02
6.17912	4.88E-02
4.99404	4.49E-02
3.54056	3.78E-02
2.45056	3.15E-02
1.49881	2.50E-02
0.85259	2.11E-02
0.38412	1.85E-02
0.14203	1.70E-02

[0101] From the results shown in Table 20 and Fig. 20, it was

found that the hydrogen storage rate was increased as the hydrogen pressure was increased. Even when the pressure was reduced from near 8 MPa, the storage rate is not lowered. From this, it was found that the hydrogen storage is achieved not only by physical absorption. This is attributed to the fact that hydrogen molecules are enclosed into the solid chitosan so as to form hydrogen clathrate.

[0102] We confirmed that stored hydrogen can be emitted under condition of 50 °C and the ambient pressure or under condition of a reduced pressure (0.005 MPa).

EXAMPLE 21

[0103] 0.5922g of tri-m-tolyphosphine (hereinafter, referred to as "TTP") in solid power state was evaluated according to the aforementioned test method under such a condition that the retention time at each pressure was 1 hour. The relation between the balanced pressure and the hydrogen storage rate was shown in Table 21 and Fig. 21.

Table 21

Evaluation Results of Hydrogen Storage Capacity of TTP

(25°C; Retention time at each pressure: 1 hour)

Balanced Pressure (MPa)	Hydrogen Storage Rate (wt%)
0.00001	0
0.30448	6.50E-03
0.70533	1.06E-02
1.72793	2.40E-02
2.74021	3.75E-02
3.552	4.73E-02
4.65216	6.82E-02
8.05616	1.25E-01
6.27169	1.15E-01
4.81187	9.71E-02
3.85328	8.07E-02
2.56244	5.96E-02
1.53375	4.23E-02
0.86878	3.32E-02
0.38471	2.73E-02
0.13945	2.45E-02

[0104] From the results shown in Table 21 and Fig. 21, it was found that the hydrogen storage rate was increased as the hydrogen pressure was increased. We confirmed that stored hydrogen can be emitted under condition of 50 °C and the ambient pressure or under condition of a reduced pressure (0.005 MPa).

[0105] As apparent from the aforementioned results, according to the method for storing hydrogen of the present invention, hydrogen can be stored at the ordinary temperature and the ambient pressure, thereby eliminating the necessity of a pressure tight vessel, a cryogenic vessel, and the like. Therefore, the storage and transport of hydrogen in relatively compact and light form is be achieved and, in addition, stored hydrogen can be easily emitted and used for various applications.

[Description of hydrogen clathrate and production method

thereof]

[0106] Now, a hydrogen clathrate and a production method thereof of the present invention will be described in detail.

[0107] In the hydrogen clathrate and the production method thereof of the present invention, there is no particular limitation on host compound so that the host compound for enclosing hydrogen is any of compounds capable of enclosing hydrogen. Known host compounds are organic compounds of monomolecular type, multimolecular type, high-molecular type, and the like as described with regard to the method of hydrogen storage of the present invention and inorganic host compounds. Examples of the inorganic host compounds include clay minerals, montmorillonites, and zeolites.

[0108] Among the above host compounds, host compounds of multimolecular type of which enclosure capacity is hardly influenced by the size of molecules of guest compound are preferable. Among host compounds of multimolecular type, phenol-based host compounds such as 1,1-bis(4-hydroxyphenyl)cyclohexane are advantageous in view of enclosure capacity and industrial ready availability.

[0109] As the method of producing a hydrogen clathrate by making hydrogen to be enclosed by such a host compound, there are the following methods:

1. Method of dissolving a host compound into a solvent and bringing hydrogen in contact with the dissolved host compound during the recrystallization;

2. Method of bringing hydrogen and a host compound directly in contact with each other (for example, as stated in the description about the method of hydrogen storage, a method of bringing hydrogen and a host compound in contact with each other

in the pressurized state);

3. Method of directly reacting a host compound with hydrogen by pulverizing the host compound in hydrogen atmosphere;

and the like. To insert hydrogen molecules into crystal lattice of the host compound, it is preferable to dissolve a host compound to a solvent, dispersing molecules of the host compound, and after that reacting the host compound with hydrogen as guest molecules during the recrystallization because such a method enables to effectively produce a hydrogen clathrate.

[0110] In this case, the solvent for dissolving the host compound may be any of solvents capable of dissolving the host compound and is suitably selected according to the kind of the host compound. For example, any of solvents including alcohols such as methanol and ethanol, ketones such as acetone and methyl ethyl ketone, esters such as ethyl acetate, ethers such as diethyl ether and dibutyl ether, furans such as etrahydrofuran, amides such as dimethyl acetamide, and aldehydes such as acetaldehyde and benzaldehyde can be employed as a solvent for a host compound of multimolecular type such as a phenol-based host compound as mentioned above. Among these, high volatile solvents are preferable. In addition, it is preferable to use a solvent which is not enclosed by the used host compound (because, if using a solvent which can be enclosed by the used host compound, hydrogen, taken off from the obtained hydrogen clathrate, may unfortunately contain the solvent). However, there is a case that three components, i.e. a host compound, hydrogen and solvent, cooperate together to form a stable clathrate, so the solvent is thus not limited the aforementioned condition.

[0111] There is no particular limitation on the concentration

of the host compound in the solvent because the solubility depends on the kind of host compound and the kind of solvent.

[0112] To bring the host compound dissolved in solvent and hydrogen in contact with each other, hydrogen is injected into the solvent with bubbling. Therefore, the host compound in the solvent comes in contact with hydrogen to react with the hydrogen and the solvent is vaporized, thereby depositing crystals of hydrogen clathrate enclosing hydrogen molecules as guest molecules. This reaction can occur at the ordinary temperature and at the ambient pressure.

[0113] The hydrogen clathrate obtained in the aforementioned manner is a hydrogen clathrate normally having hydrogen molecules from 0.2 to 20 moles relative to 1 mole of the host compound, but somewhat depends on the kind of used host compound and the contact condition with hydrogen.

[0114] The hydrogen clathrate thus obtained can stably enclose hydrogen for a long period of time at the ordinary temperature and the ambient pressure. Moreover, the hydrogen clathrate is light as compared to hydrogen storage alloy and thus has excellent handling property. In addition, the hydrogen clathrate can be easily stored and transported in a container made of glass, metal, or plastic.

[0115] Further, the hydrogen can be taken off from the hydrogen clathrate by heating the hydrogen clathrate to a temperature in a range from 30 °C to 200 °C, particularly in a range from 40 °C to 100 °C. The temperature somewhat depends on the kind of host compound. Accordingly, hydrogen can be easily emitted from the hydrogen clathrate and collected.

[0116] Hydrogen clathrate produced by injecting hydrogen into a solvent containing dissolved host compound as mentioned

above normally consists of two components of the host compound and the hydrogen. However, there is a case that the hydrogen clathrate includes used solvent in addition to host compound and hydrogen, that is, consist of three components of the host compound, the hydrogen, and the solvent. To prevent the solvent from being emitted together with the hydrogen while the hydrogen is taken off from the hydrogen clathrate consisting of the three components, it is preferable that the hydrogen clathrate has a difference of 20 °C through 30 °C between the emission temperature of solvent and the emission temperature of hydrogen. In this case, it is especially preferable that the used solvent having a boiling point higher than the emission temperature of the hydrogen.

[0117] The host compound after emitting hydrogen once enclosed therein can form a hydrogen clathrate enclosing hydrogen again by being in contact with hydrogen again. That is, the host compound is reusable repeatedly. Further, the host compound in solid state after emitting hydrogen once enclosed therein has improved selective enclosure capacity of hydrogen so that even when the host compound reacts with mixed gas containing hydrogen, the host compound selectively encloses hydrogen.

[0118] With such a host compound having improved selective enclosure capability of hydrogen, only hydrogen can be selectively collected from various process exhaust gas containing hydrogen, thereby making an effective use of collected hydrogen as energy resource.

[0119] The hydrogen clathrate and the production method thereof of the present invention will be described in detail with reference to Examples.

EXAMPLE 22

[Production of Hydrogen Clathrate]

[0120] 0.2g of 1,1-bis(4-hydroxyphenyl)cyclohexane (hereinafter, referred to as "BHC") and 3ml of methanol were put in a sample bottle and mixed so that the BHC was dissolved. As hydrogen was bubbled from a commercially available gas cylinder into the solvent, the methanol as solvent evaporates, thereby obtaining crystals. These crystals were air-dried for 1 hour under room temperature to vaporize the methanol (Crystal A).

[0121] For comparison, a solvent obtained by dissolving 0.2g of BHC in 3ml of methanol was left without reaction (with hydrogen). Crystals thus deposited were taken (Crystal B).

[0122] The IR spectrum measurements were made on Crystals A and B obtained above. The results of the measurements are shown in Figs. 20 and 21, respectively, and the superposed data of these results is shown in Fig. 22. From Figs. 20 through 23 showing IR spectrums, the IR spectrums of the crystal A and Crystal B are clearly different from each other in a range from 3100 to 3700 cm^{-1} and around 1200 cm^{-1} depending on the hydrogen group of BHC as the host compound. This makes sure that different crystals were obtained.

[0123] In addition, TG-DTA measurements were made on the two different crystals. The measurement conditions were a temperature range from 25 °C to 500 °C and a temperature increasing rate of 10 °C/minute. The result of Crystal A is shown in Fig. 23 and the result of Crystal B is shown in Fig. 24. As a result, it was found that Crystal B has a component (it may be methanol) which evaporates in a temperature range of 80 °C to 110 °C and Crystal A has components which evaporate in two

stages of a temperature range less than 50 °C and a temperature range around 80 °C. This means that Crystal A has a component which evaporates in a temperature range less than 50 °C and which was not found in Crystal B.

[0124] From these results, we can estimate that Crystal A is a clathrate consisting of three components of BHC (as the host compound)-hydrogen-methanol (BHC/hydrogen/methanol = 1/10/1 (mole ratio)) and that hydrogen is emitted at a temperature of around 40 °C to 50 °C.

[Validation of Characteristics of Hydrogen Clathrate]

(1) After the produced hydrogen clathrate (Crystal A) was put on a glass container and was left at ordinary temperature and ambient pressure for two days, IR spectrum measurement and TG-DTA measurement were conducted again. The results were almost the same as the results of the measurements before being left. It was confirmed that hydrogen can be stably stored.

(2) As the produced hydrogen clathrate (Crystal A) was put in a glass container and heated in hot water bath to a temperature of 50 °C, hydrogen was emitted, whereby 0.06g of hydrogen could be collected from 1g of hydrogen clathrate. This rate shows that 10 moles of hydrogen is enclosed relative to 1 mole of BHC.

(3) After crystals formed as a result of emission of hydrogen in (2) were dissolved in methanol in the same manner as mentioned above, hydrogen was bubbled and the methanol as solvent was vaporized so as to obtain crystals. These crystals were air-dried in the same manner as Example 20. After that, IR spectrum measurement and TG-DTA measurement were conducted. The results were almost the same as the results of the measurements of Crystal A. It was confirmed that it is possible to enclose and store hydrogen again.

(4) As the hydrogen clathrate formed as a result of enclosure of hydrogen in (3) was heated in the same manner as (2), hydrogen was emitted, whereby 0.06g of hydrogen could be collected from 1g of hydrogen clathrate.

[0125] From these results, it was confirmed that the host compound after emitting hydrogen once enclosed therein can enclose hydrogen in substantially the same amount again and can emit the hydrogen again.

[0126] As described in detail, the hydrogen clathrate and the production method thereof of the present invention can exhibit the following excellent effects:

i) can store hydrogen at ordinary temperature and at ambient pressure;

ii)can store and transport hydrogen in relatively compact and light form, without necessity of a pressure tight vessel, a cryogenic vessel, and the like;

iii) can emit stored hydrogen at a relatively low temperature around 50 °C;

iv) can store hydrogen not only from hydrogen gas but also from mixed gas by the selective enclosure of hydrogen molecules in the mixed gas;

v) can reuse host compound after enclosed hydrogen is emitted by heating because the host compound reacts with hydrogen by contact to form a hydrogen clathrate again;

vi) achieve the selective storage of hydrogen only by bring the host compound in contact with mixed gas containing hydrogen because the host compound after enclosed hydrogen is emitted by heating has improved selective enclosure capacity; and

vii) can collect hydrogen as energy resource from such hydrogen containing gas that is produced in various industrial processes

and, in the present circumstances, is discharged out of a system after being diluted, just by bringing host compound in contact with the gas.